The Global Phosphorus & Nitrogen Cycles, and Linked C-N-P Cycles
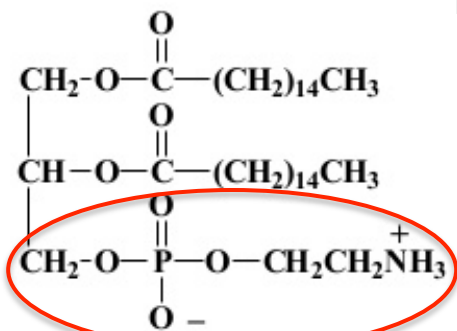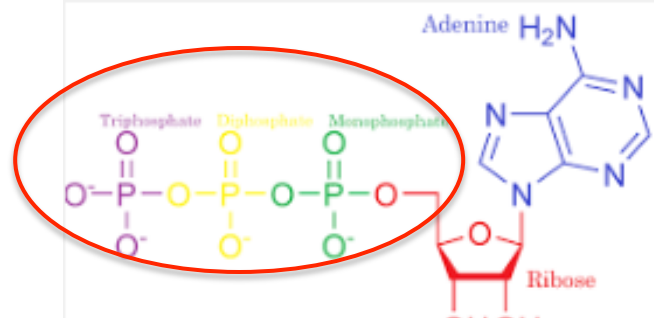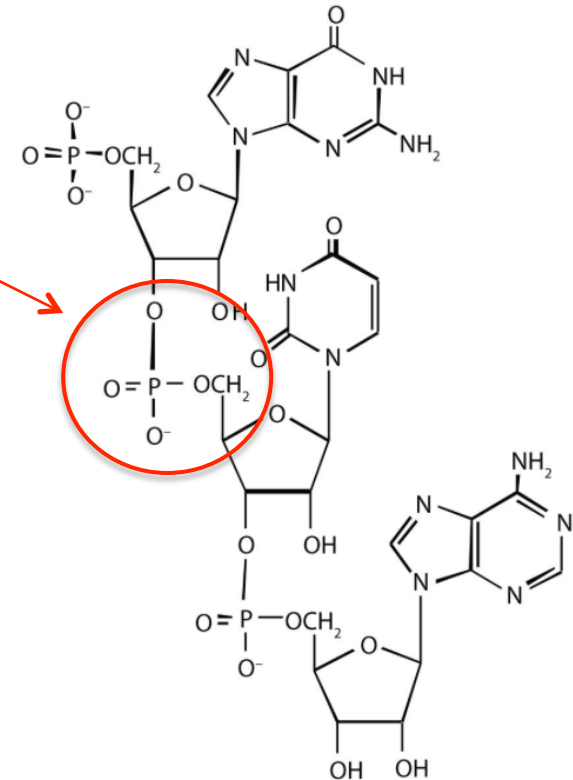
- The Phosphorus Cycle
    - Forms and Reactions
    - Reservoirs, Fluxes and Budgets

- The Nitrogen Cycle
    - Forms and Reactions
    - Reservoirs, Fluxes and Budgets

- Linkages between the Global C-N-P cycles

Basic Phosphorus Facts - 1

- ## An essential (limiting) nutrient:

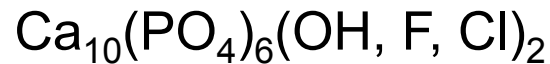 - **Genetic material (DNA, RNA)**

  - **Energy carrying compounds (ATP)**

  - **Structural support (phospholipids, bones)**

Basic Phosphorus Facts - 2

- **Apatite:**

  $$Ca_{10}(PO_4)_6(OH, F, Cl)_2$$

  - Main primary P-bearing crustal mineral

  - Hydroxy form makes up bones, teeth

- **Weathering** by naturally occurring acids derived from microbial activity:

  ❖ acid hydrolysis and/or chelation of Ca^{2+}
  ❖ congruent dissolution

- **Crustal average P concentration**: 0.076% (11th most abundant element)

- **Biological cycling:** Dissolved inorganic P in its simplest form, orthophosphate (PO_4^{3-}), is directly taken up by plants, returned to soil as organic P

Basic Phosphorus Facts - 3

- **Four components to the Global P cycle:**

    1. Tectonic uplift and exposure of P-bearing rocks

    2. Physical erosion and chemical weathering of rocks

    3. Rivers transport dissolved and particulate P to the ocean

    4. Burial of mineral and organic P in sediments

THE GLOBAL PHOSPHORUS CYCLE
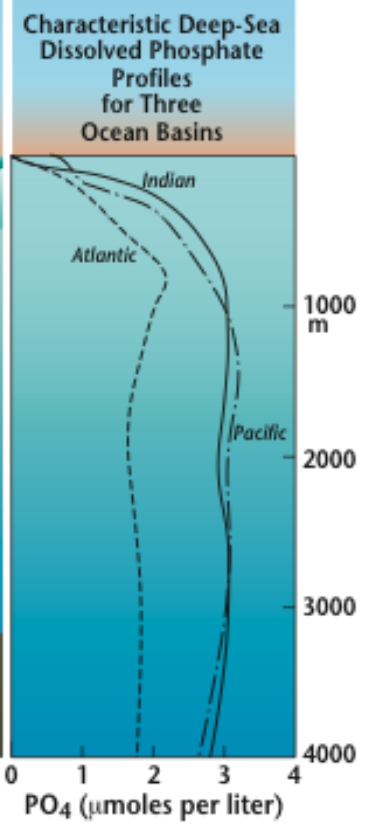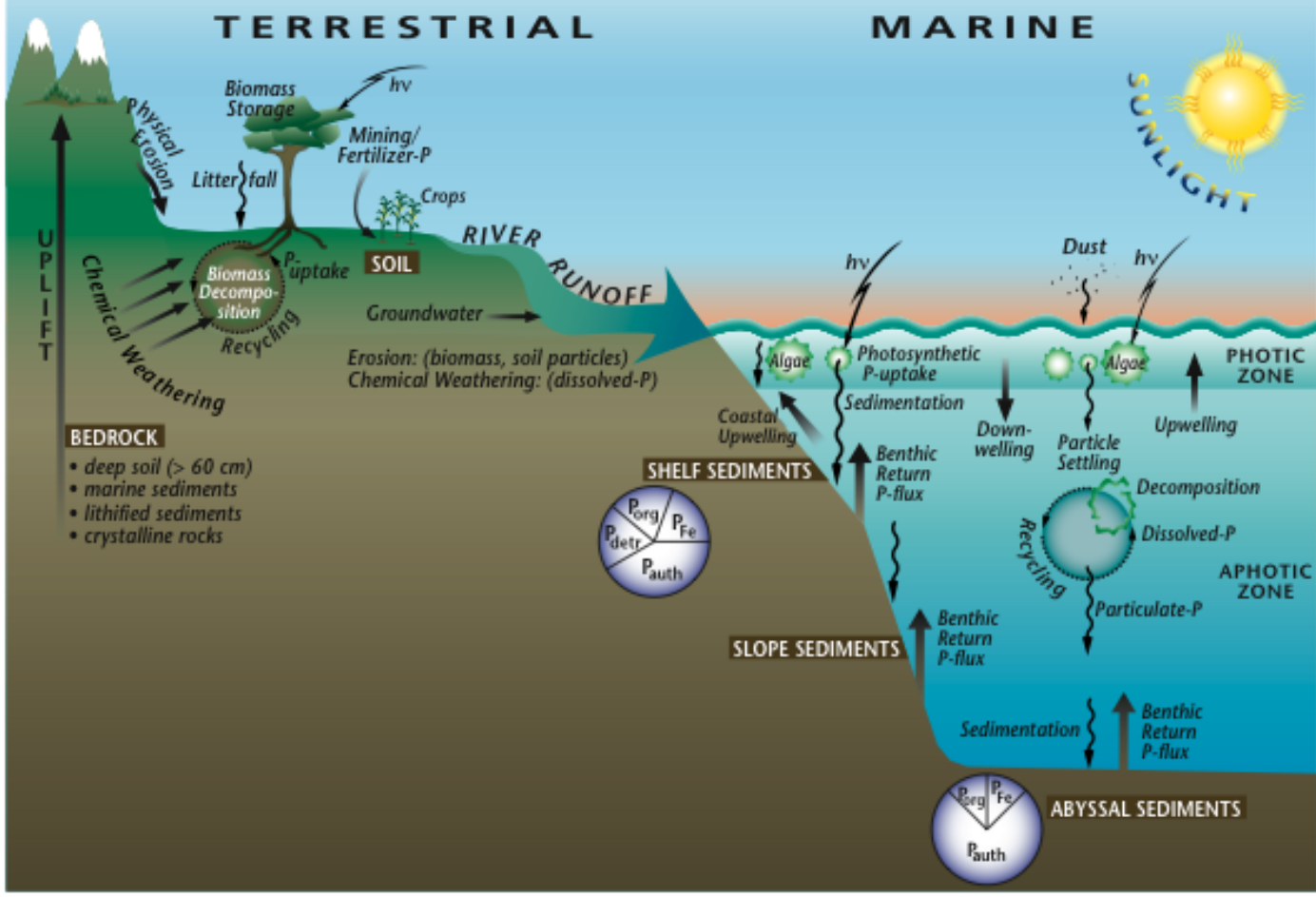
Ruttenberg, 2004, 2014

Particle Reactive P!

- Low PO_4^{3-} concentration in soil waters:

    Small $K_D = ([P]_{solution} / [P]_{solid})$

- P is sorbed efficiently by soil constituents:
    - $Al(OH)_3$
    - $Fe(OH)_3$
    - other Al- and Fe-oxyhydroxides

- Sorptive P removal impacts bioavailability to plants

- P solubility is controlled by Al at low pH and by Ca at high pH

4. The Lithosphere   99
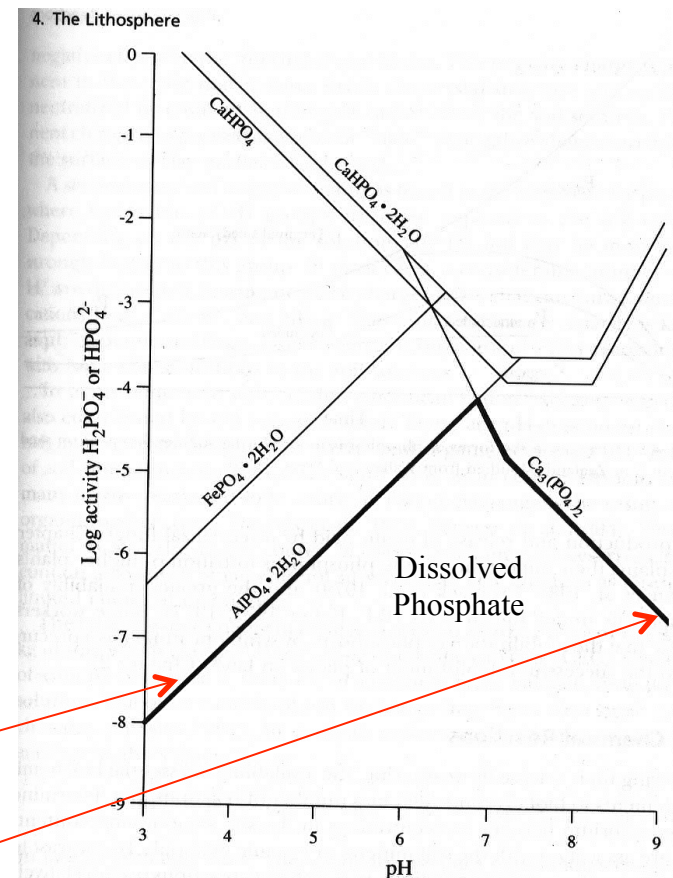
Figure 4.4 The solubility of phosphorus in the soil solution as a function of pH. Precipitation with Al sets the upper limit on dissolved phosphate at low pH (bold line); precipitation with Ca sets a limit at high pH. Phosphorus is most available at a pH of about 7.0. Modified from Lindsay and Vlek (1977).

The Phosphate - Iron Connection

- Colloidal Fe(III)-oxyhydroxides scavenge P
- Reductive dissolution of $Fe(OH)_3$ releases P
- Coupled Fe-P cycling oscillates with fluctuating redox state

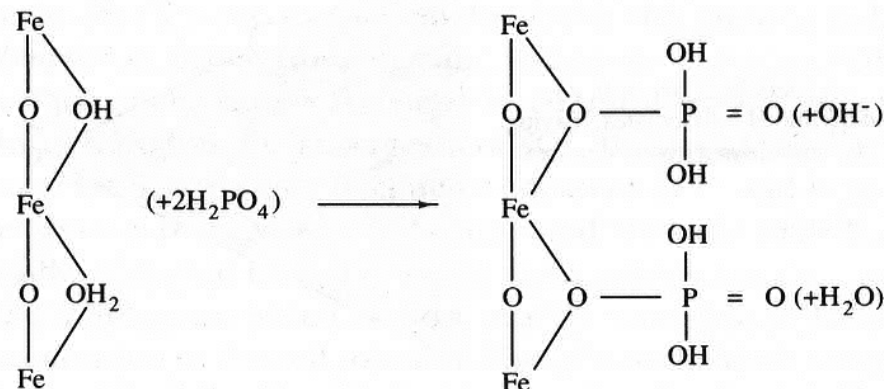**Figure 4.9** The specific adsorption of phosphate by iron sesquioxides may release OH^- or H_2O to the soil solution. From Binkley (1986).

- Al-oxyhydroxides strongly sorb P, but Al has no redox chemistry
- Clays (aluminosilicates) also sorb P

Plant Strategies to obtain P

- Increase root surface area/volume ratio

- Roots produce chelating compounds to solubilize complexed P; symbiotic fungi produce chelators

- Fungi, microbes produce enzymes / acids in the vicinity of roots that solubilize mineral-P (accelerates weathering)

- Plants reabsorb P before litterfall (recission)
  - P resides exclusively in biomass in infertile soils (laterites, bauxites, e.g., Amazon rain forest)
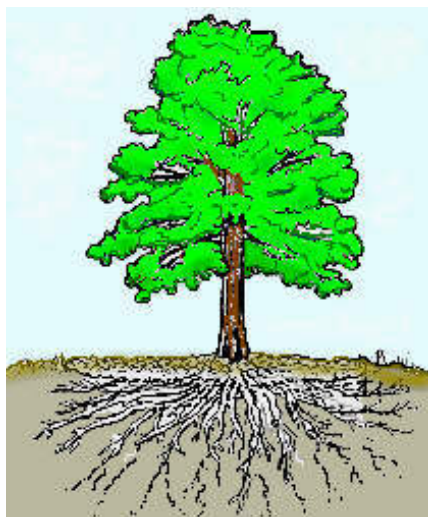
Systematic Evolution of Soil P Distribution

100% primary mineral: apatite

0% primary mineral: apatite

Refractory P

$P_{apatite}$

Terminal steady state

$P_{nonoccluded}$

$P_{occluded}$

$P_{organic}$

P_{total}

Weight of P / unit area profile

Time
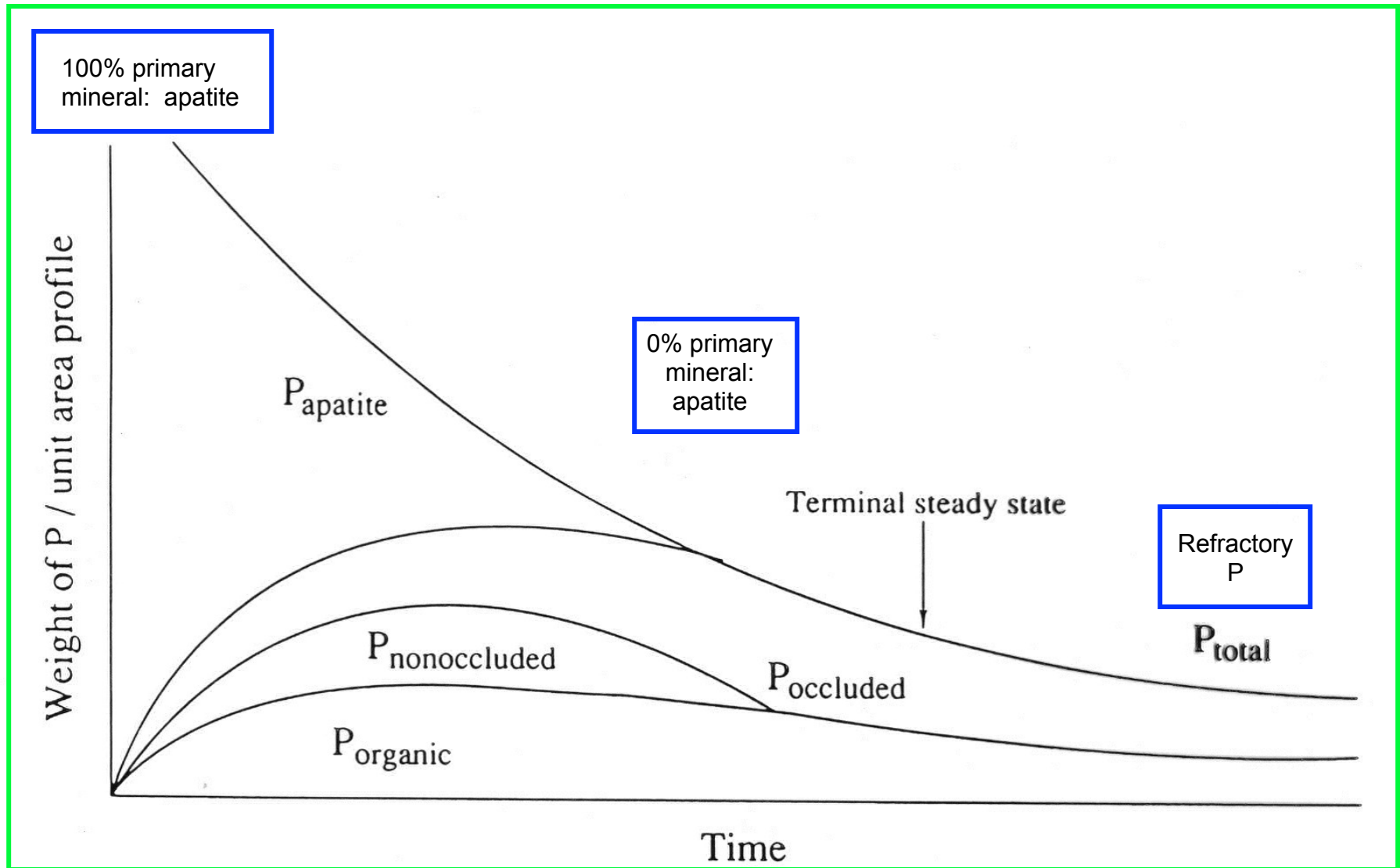
Hawaiian Islands: A Case Study of the Evolution of Soil Nutrients with Age
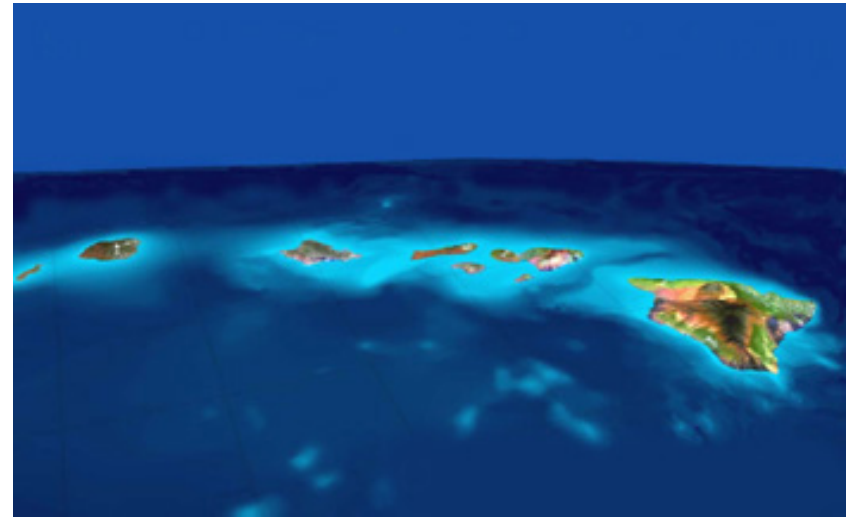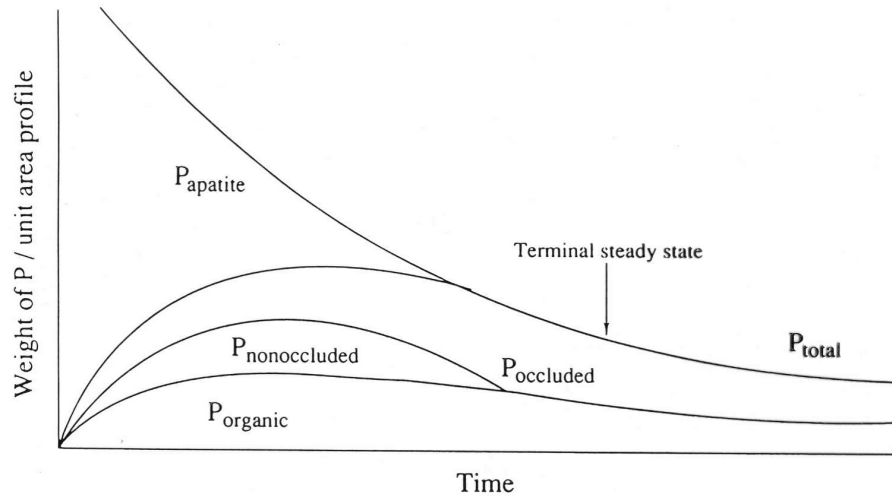
"Experimental Conditions": Same starting material (basalt)
Island age range : 0.3 to 4100 kyr

- Youngest islands: N+P limited (no soils), lots of Ca, Mg, K

- Middle-aged soils: lots of N+P, depleted cations due to weathering

- Oldest soils: minimal nutrients from soil: cations and anions from sea salt (Ca^{2+}, Mg^{2+}, K^+, NO_3^-), PO_4^{3-} from windblown dust

Chadwick et al. 1999

Atmospheric P Cycle

- Atmospheric phosphorus reservoir and fluxes are small:

  - No stable gaseous P compounds

  - Exception: Phosphine (PH_3), rare

- Main atmospheric vector:

  - P containing dust

  - Important for P-poor regions:

    o Amazon

    o Weathered Hawaiian islands

    o Oceanic gyres
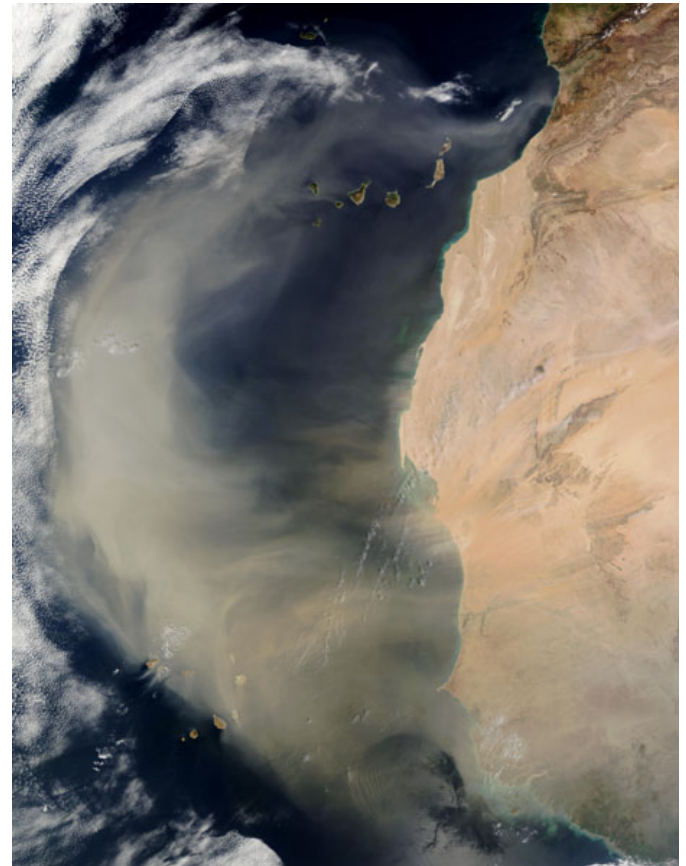
- *Oceans play a critical role in the global P cycle: terminal sink*

- *Sediments provide a paleo-record of continental and oceanic processes.*

Global Oceanic P Budget

Sources of P to the ocean:

1. Dust

2. Rivers and groundwater discharge

Sinks of P from the ocean;

1. Burial with Sediments

2. Mid-Ocean Ridges

River-Borne Phosphorus

- Riverine P flux >90% associated with particulates
  - 1° mineral: apatite
  - $Fe(OH)_3$ adsorbed P (small K_D ($[P]_{solution}$ / $[P]_{solid}$))
  - Suspended clays and Al hydroxides adsorb P
  - 20-40% organic P

- P on colloids equilibrates with dissolved phase, provides a constant low level of bioavailable P (the PO_4^{3-} Buffer Mechanism)
  - important in high turbidity rivers: e.g., Amazon, Zaire, Orinoco

- Anthropogenic activities:
  - Fertilizer mining and use has increased river P flux 50% to 3-fold
  - Deforestation leads to increased particulate transport
  - Dams can mitigate increased sediment flux by intercepting and storing
  - Can lead to eutrophication and hypoxia

P Cycling in Aquatic Systems

- Stratification -> depletion of P in surface water

- Burial of organic matter in sediments removes P from water column

- Microbial respiration of buried organic matter within sediments

      - consumes O_2
      - generates remineralized, dissolved P

- Oxic waters at sediment-water interface produce Fe oxide trap

- Anoxic diagenesis can remobilize P through reduction of Fe(III) to Fe^{2+}

- Pyrite formation at depth sequesters Fe

      - decouples Fe and P cycles,
      - allows more P to diffuse back
             into the water column

- Contrast between marine and freshwater systems:

      - Low SO_4^{2-} in lakes
      - Less FeS_2 formation than in
             marine sediments
     -More extensive coupled P-Fe
             cycling

Bloom

Water

Sediment

O_2

PO_4

$Fe(OH)_3 \longrightarrow PO_4$

PO_4

$HS^- \& H_2S + Fe(OH_3)$

oxic/suboxic

$FeS \& FeS_2$ precipitation

anoxic

anoxic
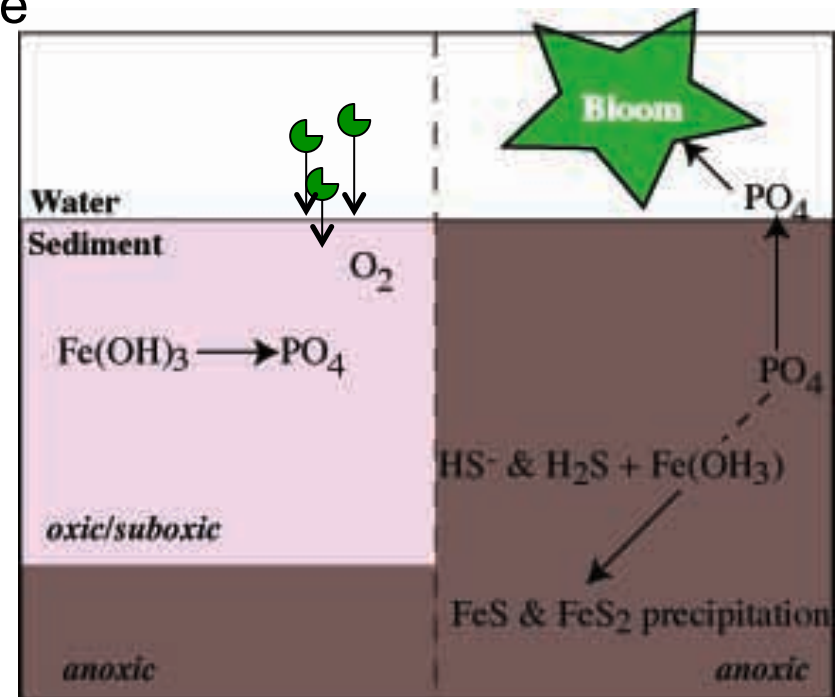
P cycling in Estuaries and Coastal Waters

- Estuarine P-**removal** mechanisms:

  - flocculation of Fe in low-salinity region of estuaries

  - flocculation of humic compounds with associated P

  - biological P-uptake

- Estuarine P-**addition** mechanisms:

  - remobilization of sorbed P on particles by displacement reactions in
         high ionic strength mixing zone of estuary
  - anoxic diagenesis in estuarine sediments $\longrightarrow$ benthic return P flux

- 25-45% of riverine particulate P may be mobilized and returned to
  the water column

- Groundwater seepage important source of P to coastal zone in
         some places

- Cultural eutrophication in coastal regions $\longrightarrow$ hypoxic zones;
   can be linked to harmful algal blooms

The Marine P Cycle

- Dominated by biological transport

- Remineralization of organic P at depth

- Accumulation in deep waters along advective flow path

- Burial of organic P in sediments occurs mostly in shallow regions

- Expansion of shelf regions during high sea level stands results in more P burial

- Oceanic P residence time varies as a function of sea level
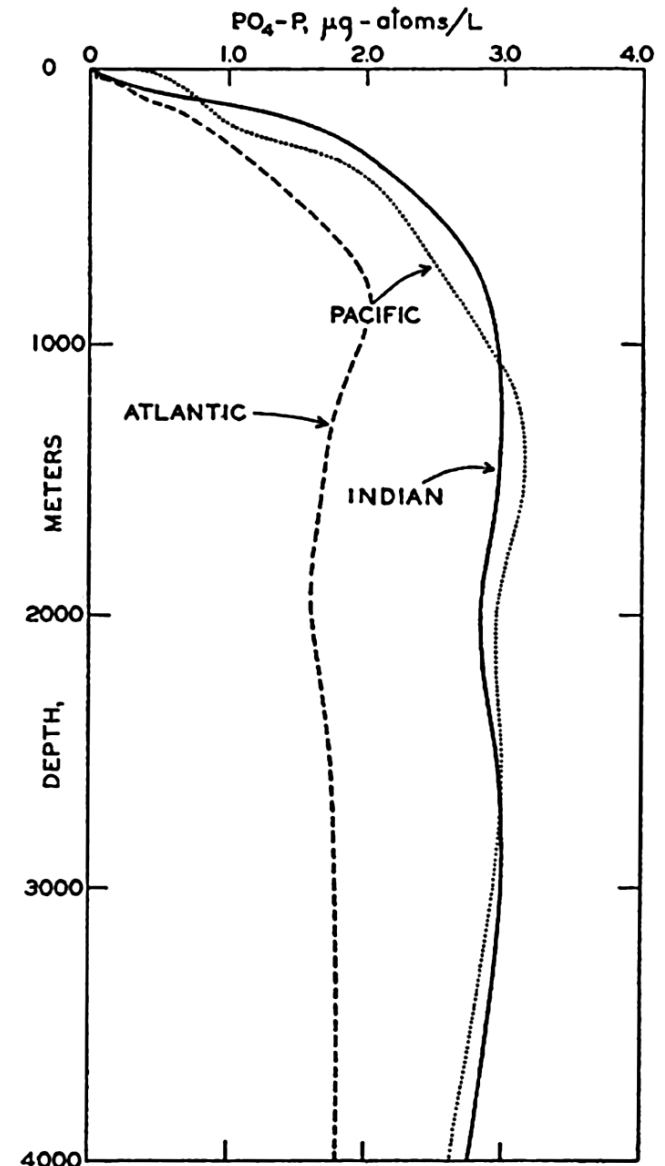
P-sinks: Authigenic-P and Organic-P

- Labile organics break down quickly, refractory organic compounds are preserved

- Fe(ox)-P and other weathered P minerals deposited and buried

- Carbonate fluorapatite forms in sediments

- In *Phosphorite* deposits P_2O_5 content reaches 5-40%

- Contrast with 0.3% in most sediments
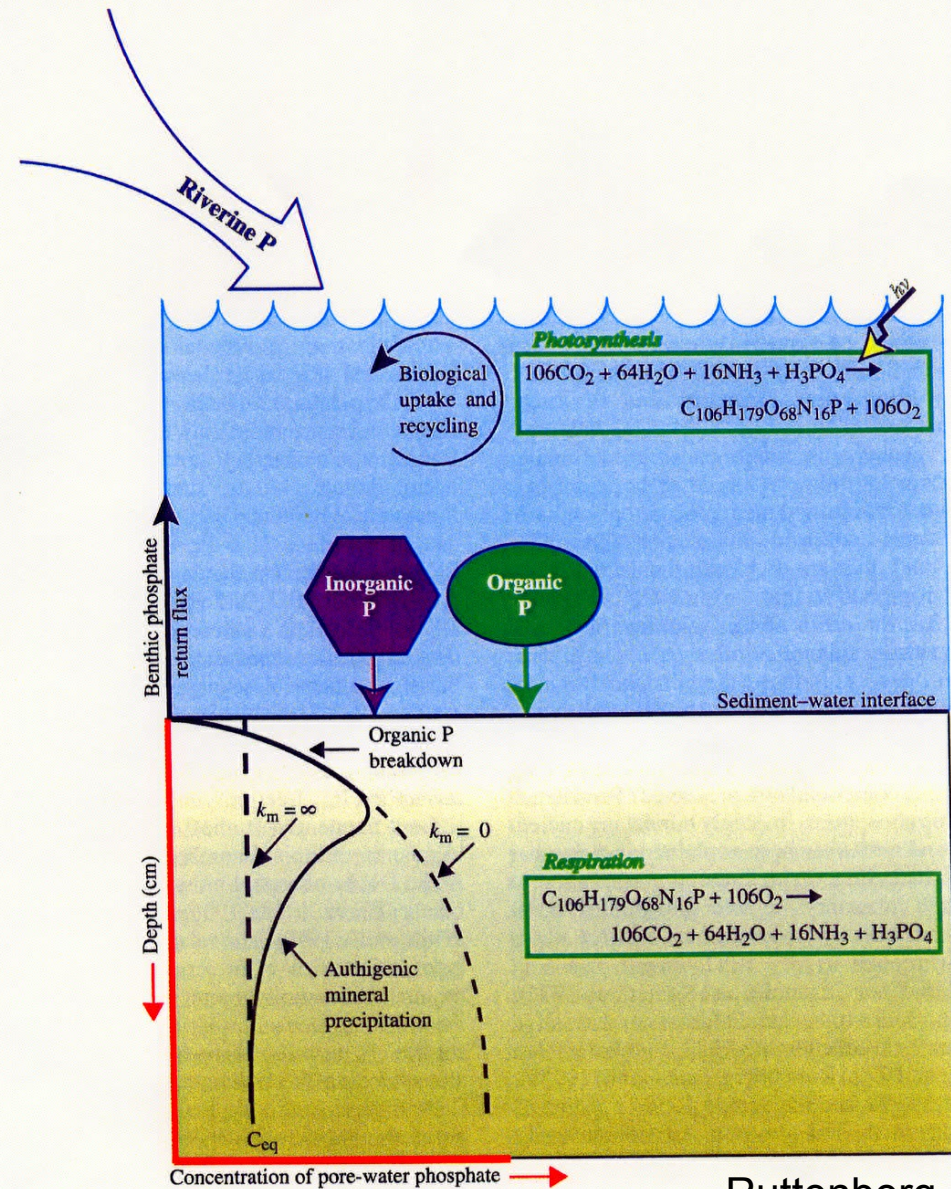
Ruttenberg (2014)

Phosphorites Through Time

- Authigenic apatite formation in marine sediments:

$$Ca_{10}(PO_4)_{6-x}(CO_3)_x F_2$$
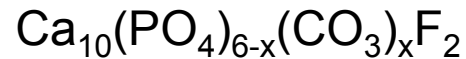
- Large changes in phosphorite accumulation imply large changes in global P cycle

- Causation linked to:
  - oceanic anoxic events?
  - continent configuration?
  - sea floor spreading rates?

- Satisfactory explanation remains elusive

P ABUNDANCE (METRIC TONS OF P_2O_5)
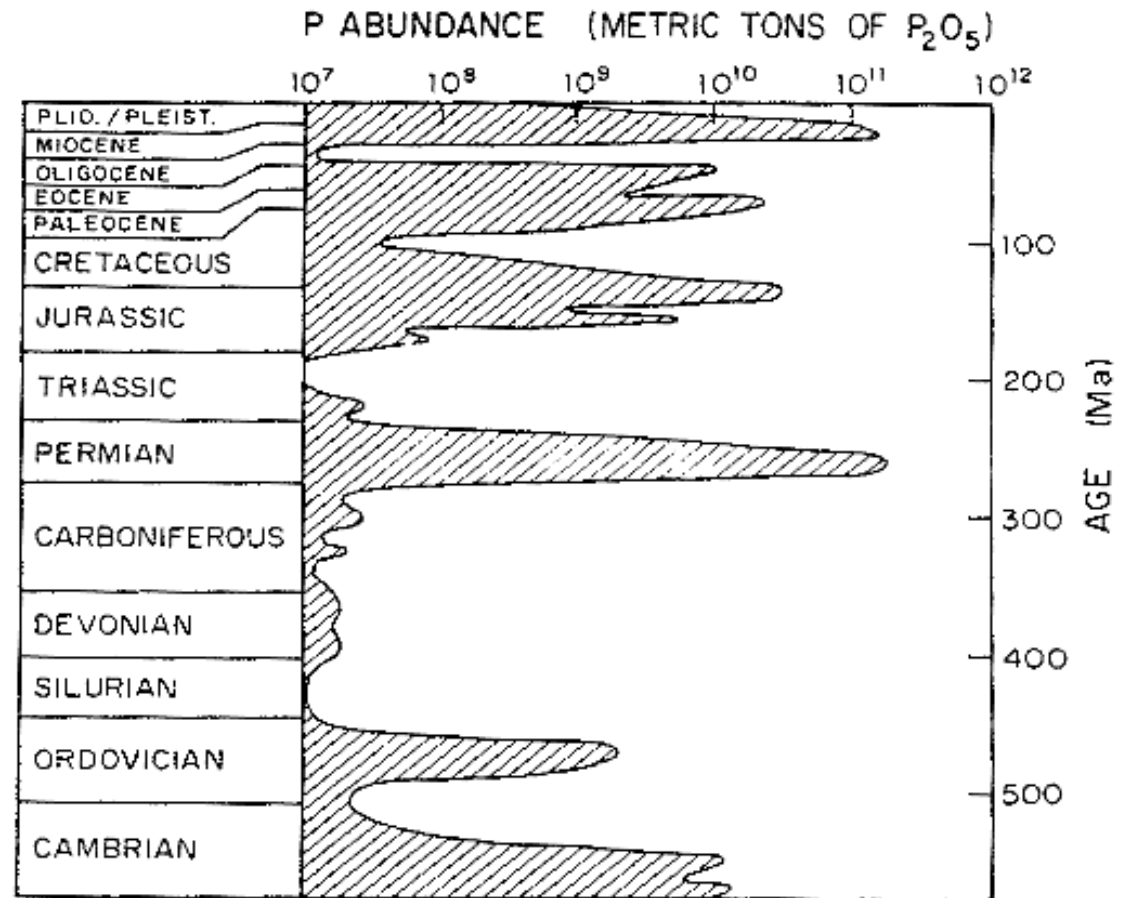
Cook and McElhinny 1979

Distribution of SOM is similar to that of NPP in surface waters, except that a greater fraction of total burial (83%) occurs on the shelf
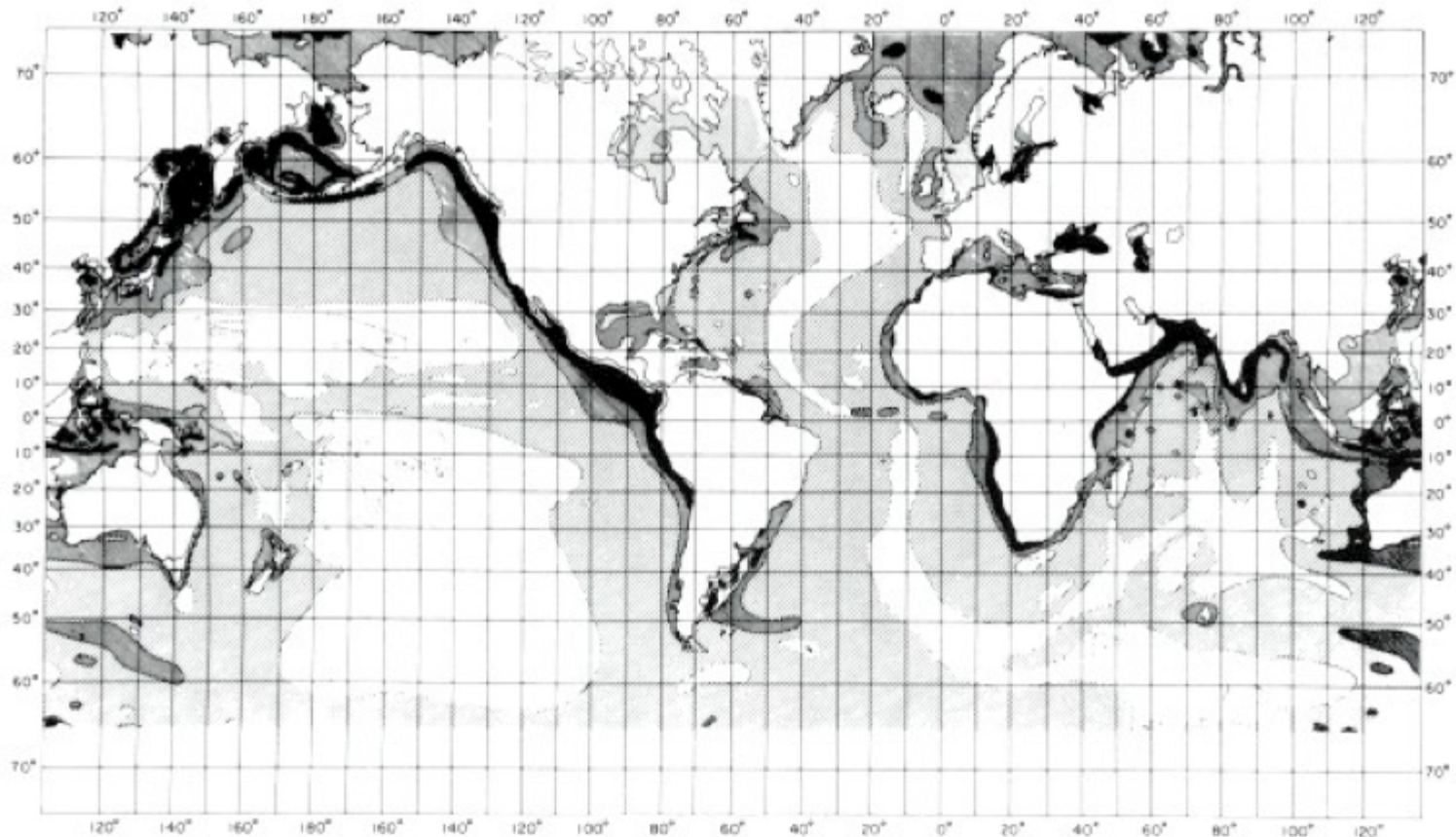
Figure 14.3 Global distribution of organic carbon (% dw) in surface sediments in five categories of > 2.00, 1.01-2.00, 0.51-1.00, 0.25-0.50, and < 0.25 (after Premuzic et al., 1982). (Reprinted with permission from *Organic Geochemistry*, 4, 1982, Pergamon Journals Ltd.). www.icsu-scope.org/.../ scope35/chapter14.html

Residence time of Phosphorus in the Oceans

- Until 1993, $T_r(P)$ estimated at 100 kyr (Broecker and Peng,1980)

- Once higher P burial rates in ocean margin sediments recognized: $T_r(P) \approx 10\text{-}17$ kyr (Ruttenberg 1993)

- Short enough for changes in P reservoirs to be a factor in glacial-interglacial CO_2 cycles

- Links P cycle to the N cycle in the ocean: have similar T_r

Oceanic P-burial and P-Residence Time Fluctuate with Sea Level

1. Sea Level High Stand

Enhanced P burial

shelf

slope

Abyssal plain

2. Sea Level Low Stand

Transport to open ocean

shelf

slope

Abyssal plain
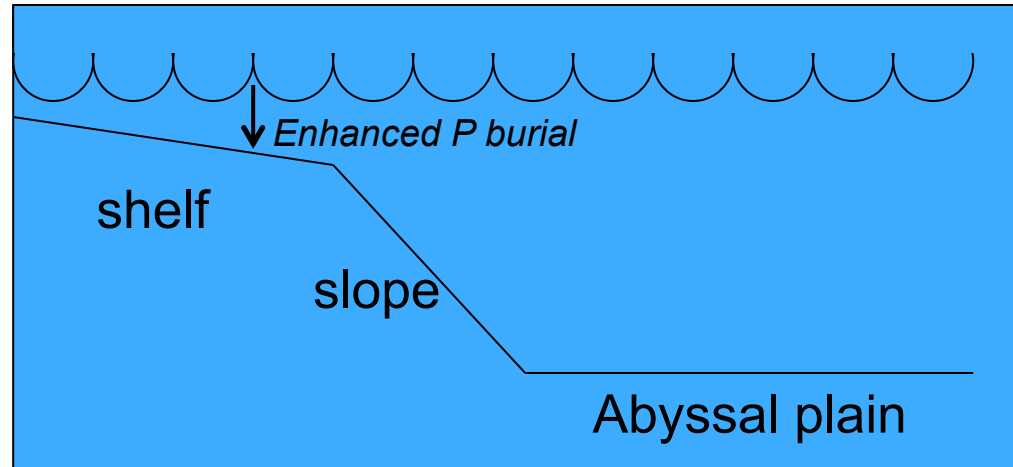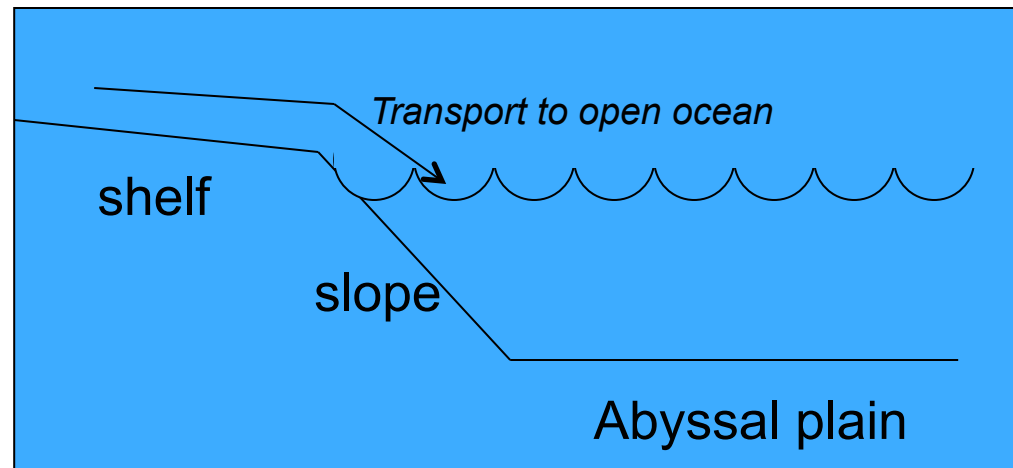
Summary: Global P-cycle

- Four components to the global P cycle

  Uplift -> Weathering -> Transport -> Burial with marine sediments

- P biogeochemistry
  - Essential nutrient
  - Particle-reactive (high K_D)
  - Cycles with Fe (impacted by redox state)

- Oceanic P sources and sinks

  - conversion of unavailable to bioavailable forms
  - modification reactions, e.g., authigenic mineral formation

- Revised Oceanic P residence time: Shorter than previously believed

Basic Nitrogen Facts - 1

Global Nitrogen Reservoirs

Reservoir	Speciation	Quantity (g N)
Atmosphere	N_2, N_2O	3.9×10^{21}
Terrestrial Biosphere	NH_3	3.8×10^{15}
Marine Biosphere	NH_3	0.5 to 3×10^7
Seawater	N_2, N_2O, NO_3^-, DON, PON	1.6×10^{14}
Oceanic Sediments	PON, NH_4	2×10^7
Terrestrial Soils	PON, NH_4	$95 - 140 \times 10^{15}$
Crustal Rocks	PON, NH_4	1.9×10^{14}

After Schlesinger and Bernhardt 2013, and Ward 2013.

Basic Nitrogen Facts - 2

- Essential (limiting) nutrient:

  - enzymes
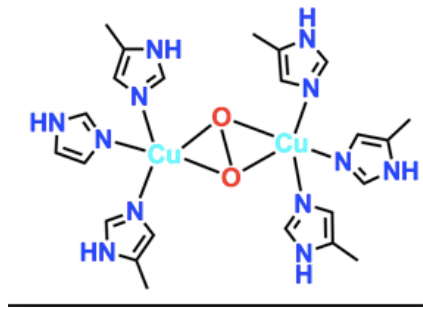
  - amino acids, proteins
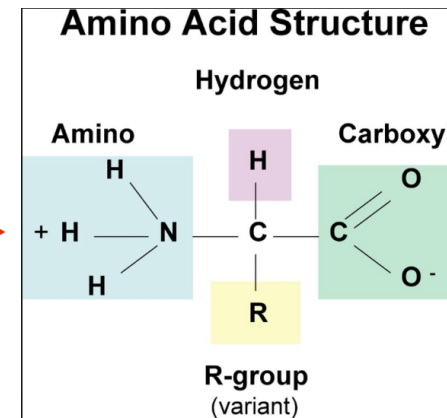
  - pigments (e.g., Chlorophyll)
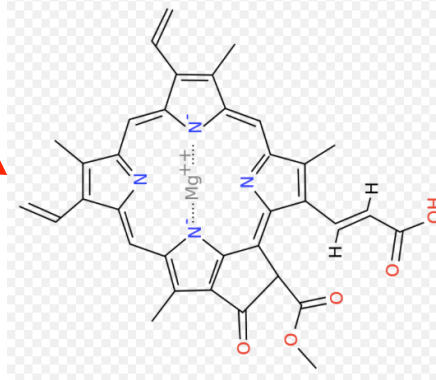
- Range of valance (oxidation) states: NH_3 (-3) to NO_3^- (+5)

  - microbes capitalize on potential transformations of N
  - utilize energy released by changes in redox potential

Basic Nitrogen Facts - 3

Microbial reactions drive the N cycle

- Nitrogen fixation:

$$N_2 + 8H^+ + 8e^- + 16\,ATP \rightarrow 2NH_3 + H_2 + 16\,ADP + 16\,P_i$$

- Nitrification:

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 4H^+$$

- Denitrification:

$$5CH_2O + 4H^+ + 4NO_3^- \rightarrow 2N_2 + 5CO_2 + 7H_2O$$

- Anammox:

$$NH_4^+ + NO_2^- \rightarrow 2N_2 + 2H_2O$$
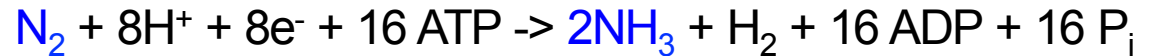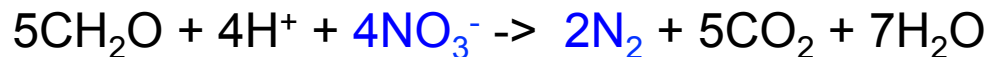
Microbial Transformations in the N Cycle
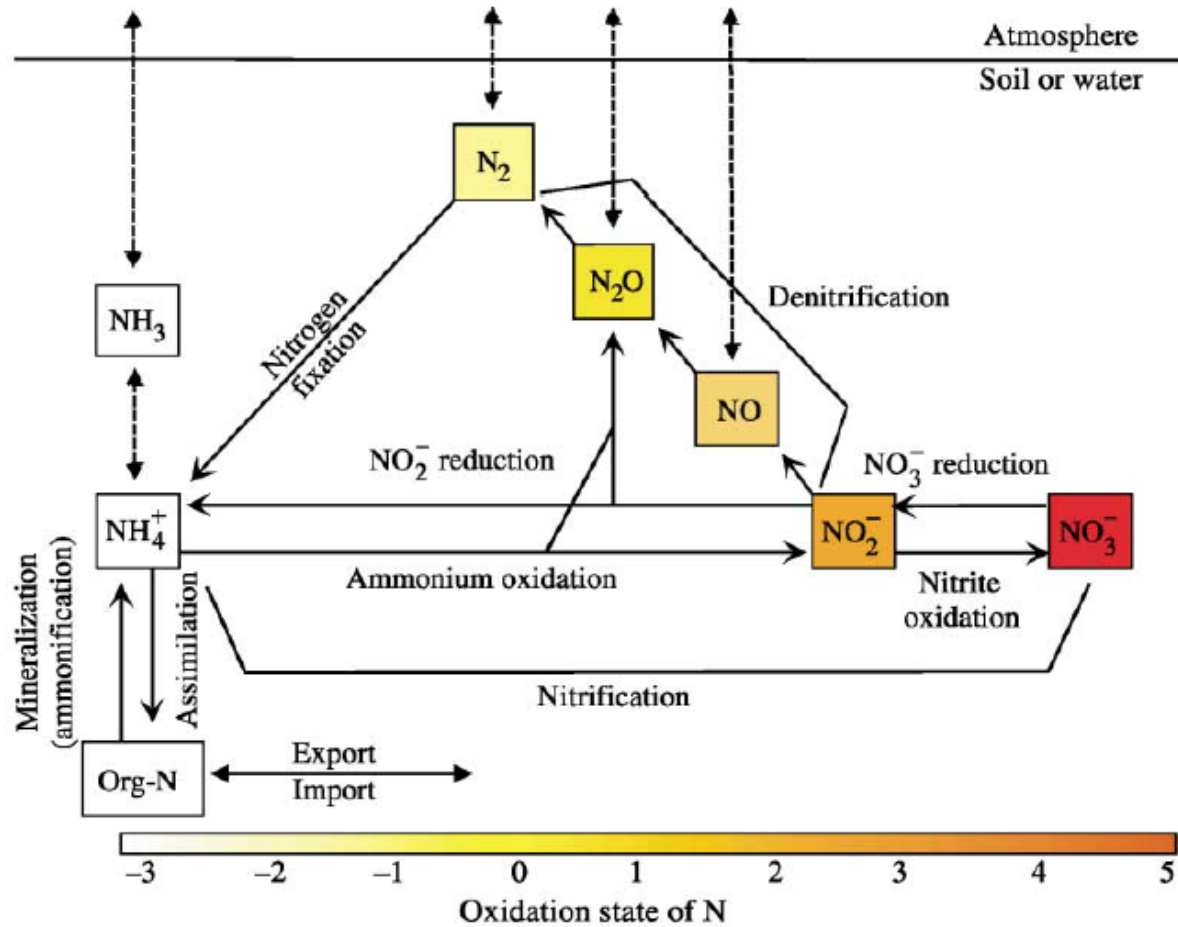
Figure 1 The processes of nitrogen fixation, assimilation, nitrification, decomposition, ammonification, and denitrification (after Karl, 2002).

Role of N in Biogeochemistry

• Bioavailability of N (and/or P) can limit NPP on land/oceans; controls size of biomass

• N has multiple oxidation states:

-3 in NH_3	ammonia
0 in N_2	nitrogen
+1 in N_2O	nitrous oxide
+2 in NO	nitric oxide
+3 in NO_2^-	nitrite ion
+4 in NO_2	nitrogen dioxide
+5 in NO_3^-	nitrate ion

• Microbial processes exploit redox gradients (for energy purposes) and thereby mediate fluxes

• Most abundant form of N is atmospheric N_2
  - N_2 is "fixed" (oxidized) by bacteria and plants in N-poor regions
  - Denitrifying bacteria reverse this process.

N-bioavailability: 'Fixed N'

- Balance of N-fixation and denitrification affects global N bioavailability:

$$N_2 + 8H^+ + 8e^- + 16\ ATP \longrightarrow 2NH_3 + H_2 + 16\ ADP + 16\ P_i$$

$$5CH_2O + 4H^+ + 4NO_3^- \longrightarrow 2N_2 + 5CO_2 + 7H_2O$$

- Pool of available inorganic N is always small; like P, bioavailable N is rapidly taken up

- All biologically available N originated as atmospheric N_2:
    - lightning
    - meteorite impacts
    - biological fixation

Nitrogen Fixation

Fig. 12.2. Units are 10^{12} g N/yr (Tg)

- Fixation in lightning < 5
- Atmosphere
- Biological fixation 120
- 160
- Human activities
- Land plants
- Denitrification 81
- Denitrification 300
- Atmospheric Deposition 67
- Soil organic - N
- 1200
- Internal cycling
- River flow 58
- Biological fixation 150
- 30
- Groundwater 18
- 8000
- Internal cycling
- Oceans
- Permanent burial 10
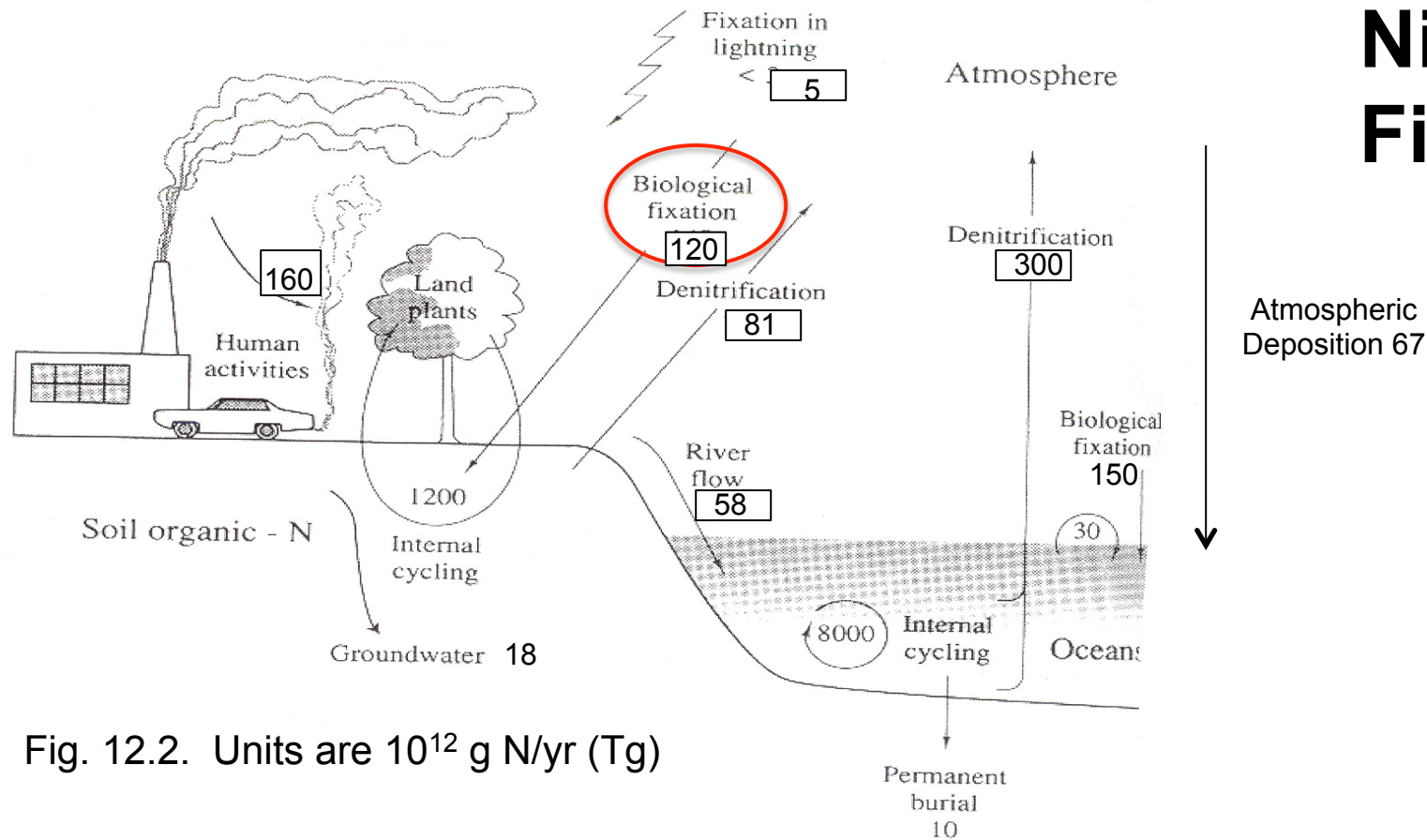
- Current terrestrial N_2-Fixation rates are dominated by biological fixation:

  - Lightning <3 - 5 x 10^{12} N yr^{-1}
  - Biological fixation 120 x 10^{12} yr^{-1}

- N $\equiv$ N triple bond takes massive energy to break

N-Fixation Pathways
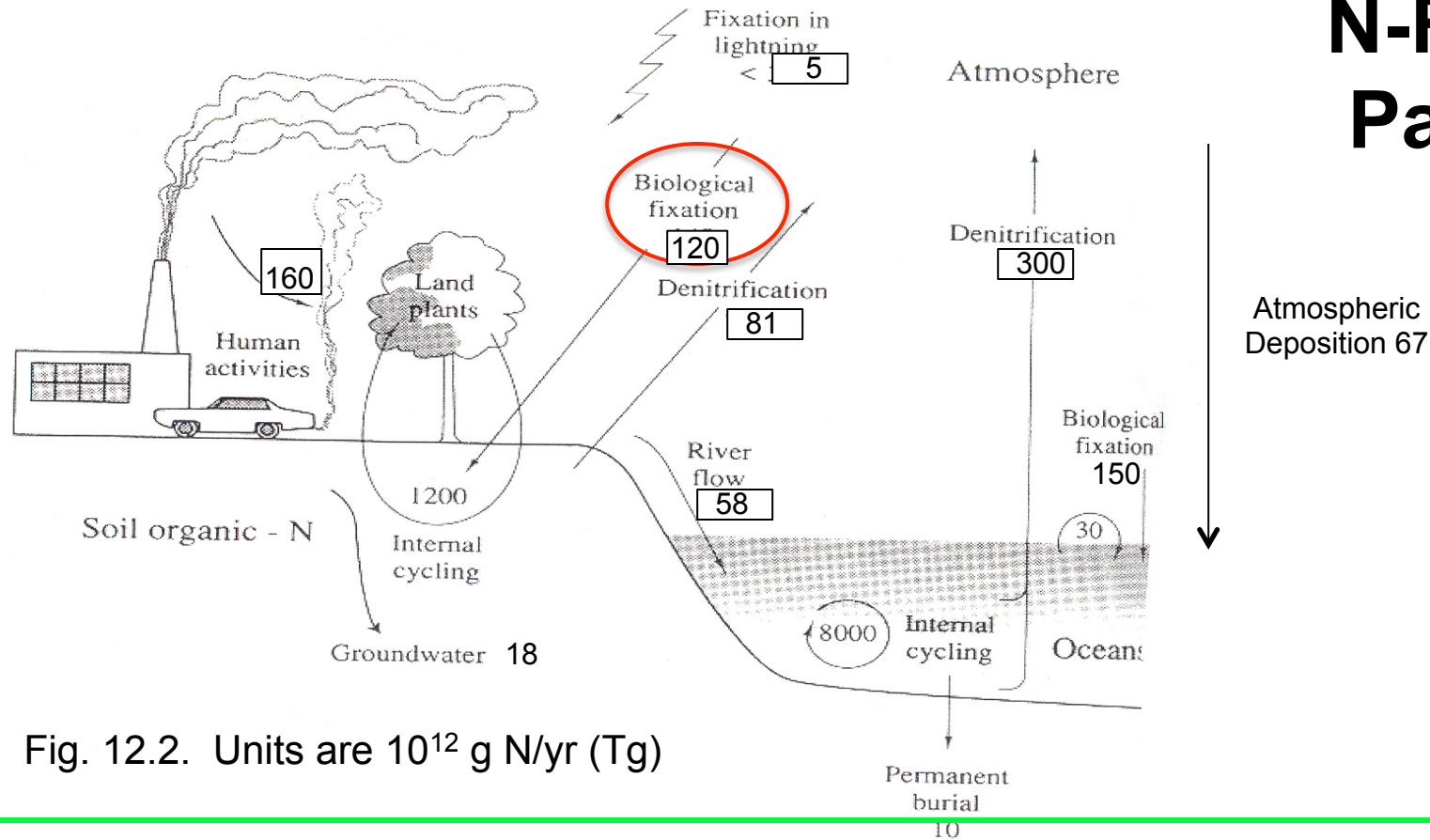

Fixation in lightning < 5

Atmosphere

Biological fixation 120

Denitrification 300

Atmospheric Deposition 67

160

Land plants

Human activities

Denitrification 81

Soil organic - N

1200

Internal cycling

River flow 58

Biological fixation 150

30

8000 Internal cycling

Oceans

Groundwater 18

Permanent burial 10

Fig. 12.2. Units are 10^{12} g N/yr (Tg)

- Total terrestrial biological N fixation ≈ 120 x 10^{12} g N yr^{-1}
- Total fixed N delivered to Earth's __land__ surface ≈ 300 x 10^{12} g N yr^{-1}
  - 28% via natural processes
  - 72 % via human-derived sources

  - > 136 x 10^{12} g N yr^{-1} from fertilizer production by the Haber process:
    natural gas (CH_4) is burned to produce H_2
    $H_2 + N_2$ (under high T and P) = NH_3

  - 25 x 10^{12} g N yr^{-1} from fossil fuel combustion

Terrestrial Nitrogen cycle

Fixation in lightning < 5

Atmosphere

160

Biological fixation 120

Denitrification 81

Denitrification 300

Human activities

Land plants

Soil organic - N

1200 Internal cycling

River flow 58

Biological fixation 150

30

8000 Internal cycling

Groundwater 18

Oceans

Permanent burial 10
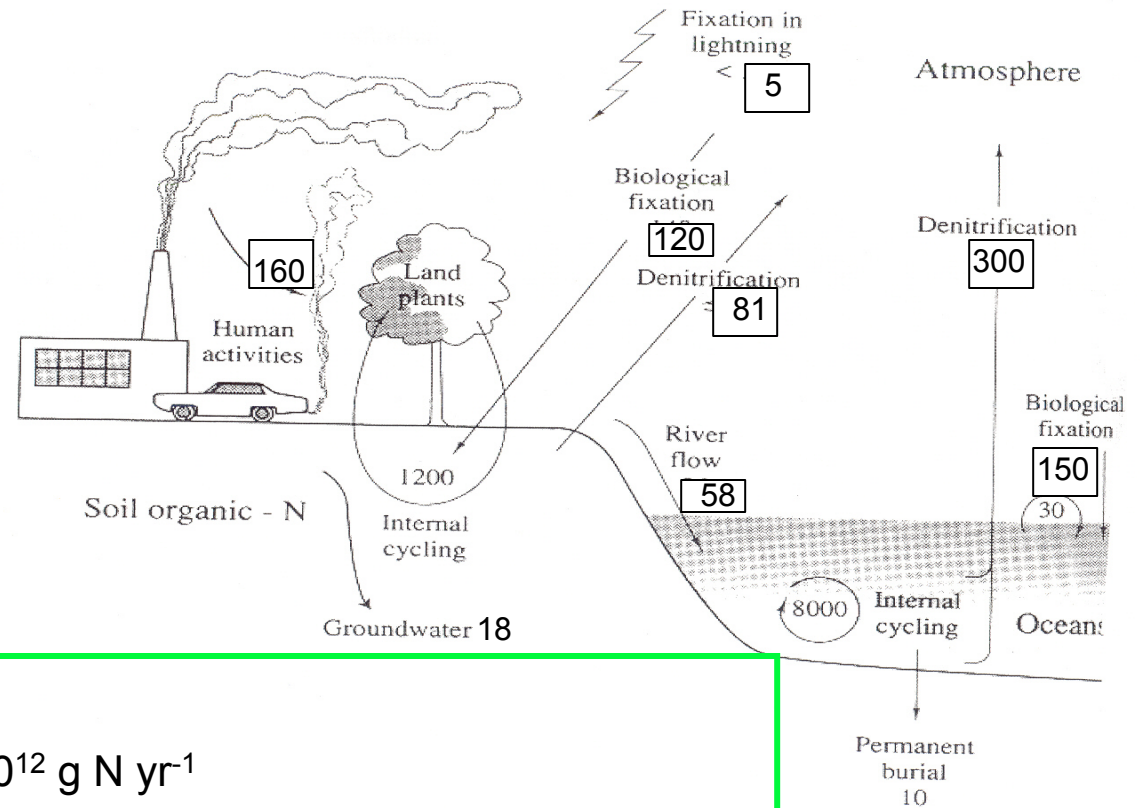
- **Allocthonous N inputs:**
  - ° Terrestrial N fixation 300×10^{12} g N yr^{-1}

- **N-removal from terrestrial soils:**
  - ° Rivers carry ~ 58×10^{12} g N yr^{-1} to the oceans
  - ° Denitrification in soils approximately balances N inputs

- Global terrestrial denitrification: $13\text{-}233 \times 10^{12}$ g N yr^{-1}
  - Wetlands account for ~50%
  - Pre-industrial denitrification $\approx 70 - 100 \times 10^{12}$ g yr^{-1}

- Denitrification produces N_2 and N_2O in a ratio of 22:1

- Biomass burning causes denitrification: ~ 37×10^{12} g N yr^{-1} (as N_2)

Oceanic Nitrogen Cycle

Fixation in lightning < 3

Atmosphere

Biological fixation 140

Denitrification ≤ 200

Denitrification 110

100

Human activities

Land plants

Atmospheric Deposition 67

Biological fixation

150

1200

River flow

58

30

Soil organic - N

Internal cycling

8000   Internal cycling

Oceans

Groundwater

Permanent burial 10
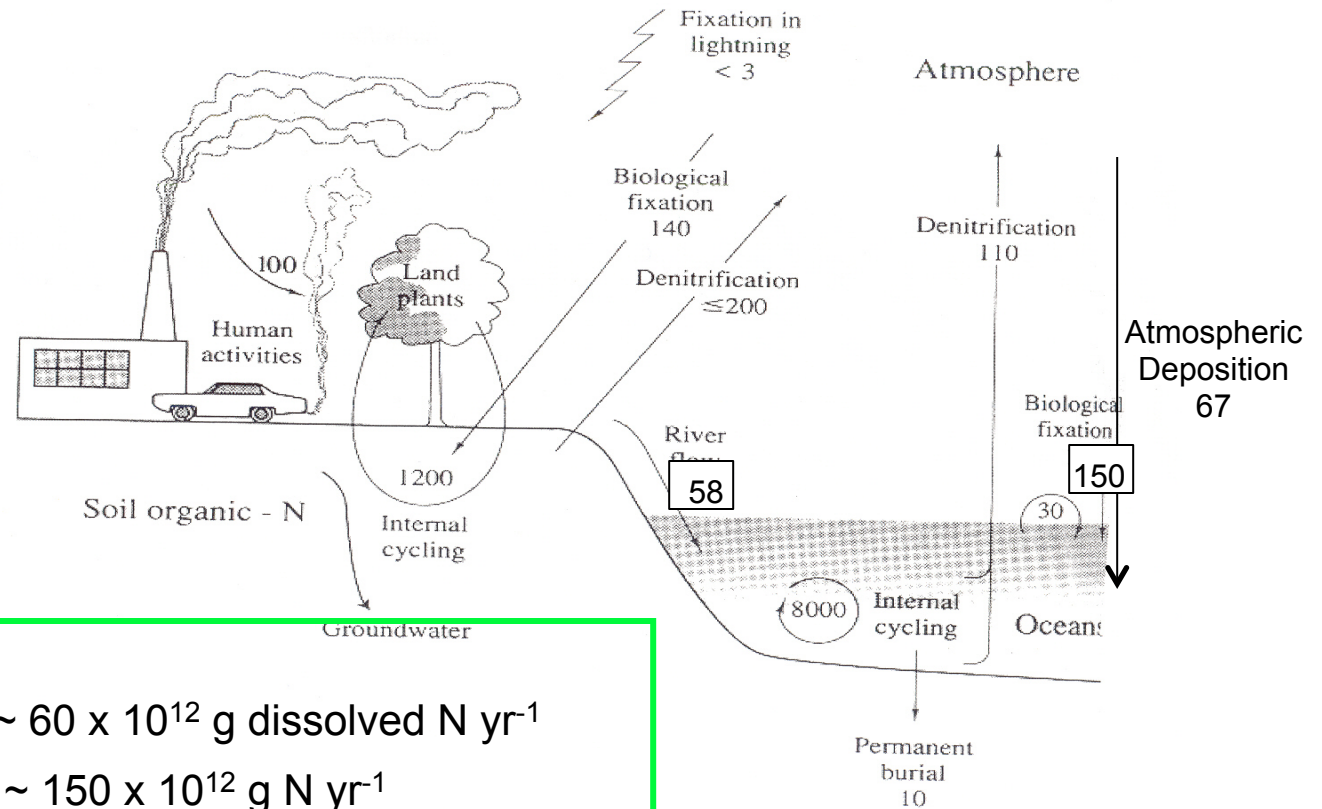
• **Allocthonous N inputs:**
   ° Rivers to oceans, ~ 60 x 10^{12} g dissolved N yr^{-1}

   ° Biological fixation, ~ 150 x 10^{12} g N yr^{-1}

   ° Precipitation, ~67 x10^{12} g N yr^{-1} (NH_4^+ and NO_3^-)

• **Autocthonous N input to surface waters:**
   ° Deep water N pool, 720 x 10^{15} g N yr^{-1}

  - Most NPP IS supported by recycling

  - Little burial of N in marine sediments

  - Oceanic N cycle closed by denitrification in low O_2 environments ~ 110-270 x 10^{12} g N yr^{-1}

Anthropogenic activity

- Planting of N fixing crops and fertilizer production (from N+H at high T) >100 x 10^{12} g yr^{-1}

- Fossil fuel combustion: ~ 25 x 10^{12} g yr^{-1}
  - produces NO_x
  - Some NO_x transported long distances -- seen in Greenland ice

- Total flux of fixed N = 240 x 10^{12} g yr^{-1}
  - 28% natural
  - 72% anthropogenic

- Groundwater N increasing from fertilizer leaching: 18 x 10^{12} g yr^{-1}

a)
— Fertilizer production
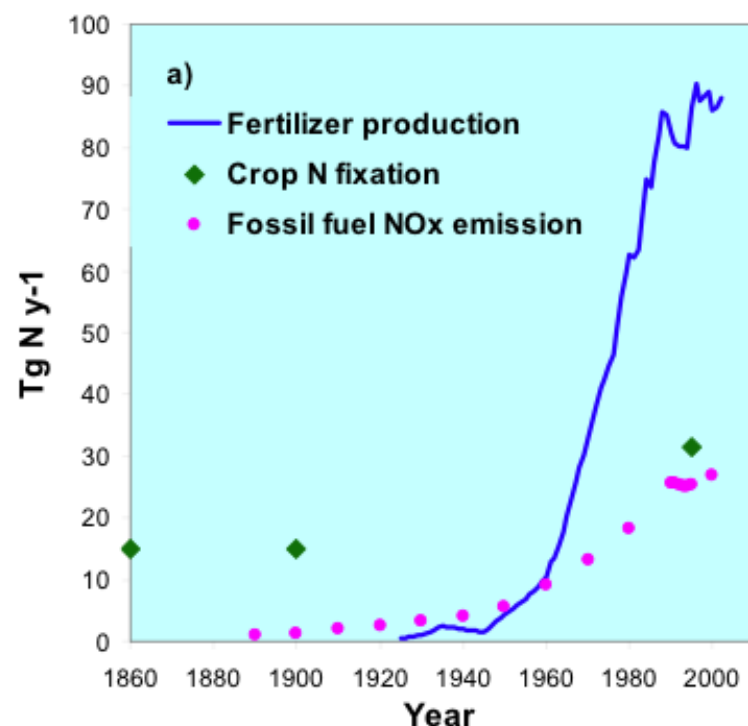◆ Crop N fixation
• Fossil fuel NOx emission

Tg N y-1

Year

Figure 1. Changes in global fluxes of reactive or biologically available N.
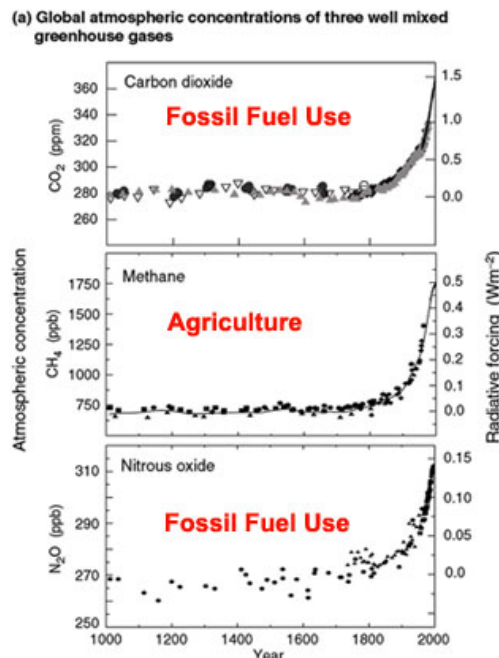
(From Holland et al., 2005 EOS 86, 254)

Nitrous oxide (N_2O)

- N_2O is a by-product of nitrogen fixation and denitrification

- N_2O is an important greenhouse gas; has **300x** the impact of CO_2, also destroys O_3

- N_2O sink: stratospheric destruction via photolysis
  - 80% $\rightarrow N_2$
  - 20% $\rightarrow$ NO, which destroys O_3

- MRT N_2O in atmosphere ~ 120 yrs -- uniformly distributed

- Seawater is a source of N_2O to the atmosphere, but some N_2O is denitrified within water column

Anthropogenic Impact on N_2O Cycle

- Soils: main source of N_2O to atmosphere,
- Cultivation increases N_2O production rate as nitrification and denitrification rates increase
- Manure production tracks N_2O increases

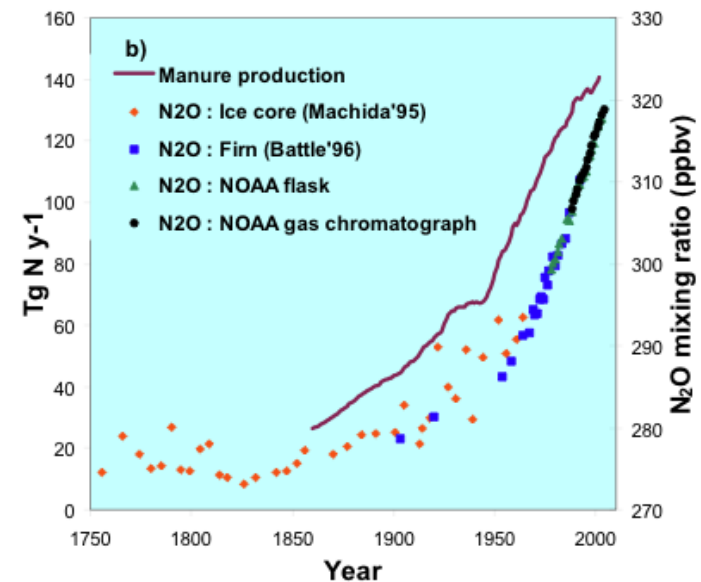From Holland et al., 2005 EOS 86, 254

(a) Global atmospheric concentrations of three well mixed greenhouse gases

Carbon dioxide — **Fossil Fuel Use**

Methane — **Agriculture**

Nitrous oxide — **Fossil Fuel Use**

b)
- Manure production
- N2O : Ice core (Machida'95)
- N2O : Firn (Battle'96)
- N2O : NOAA flask
- N2O : NOAA gas chromatograph

Figure 2. The simultaneous increase in atmospheric N_2O concentrations, and increased manure production as a result of reactive N generation in Figure 1.

- Sinks exceed identified sources, yet we observe an increase in atmospheric N_2O -- more research needed

Relationship between NO_3^- in Ice Cores and NO_x Emissions
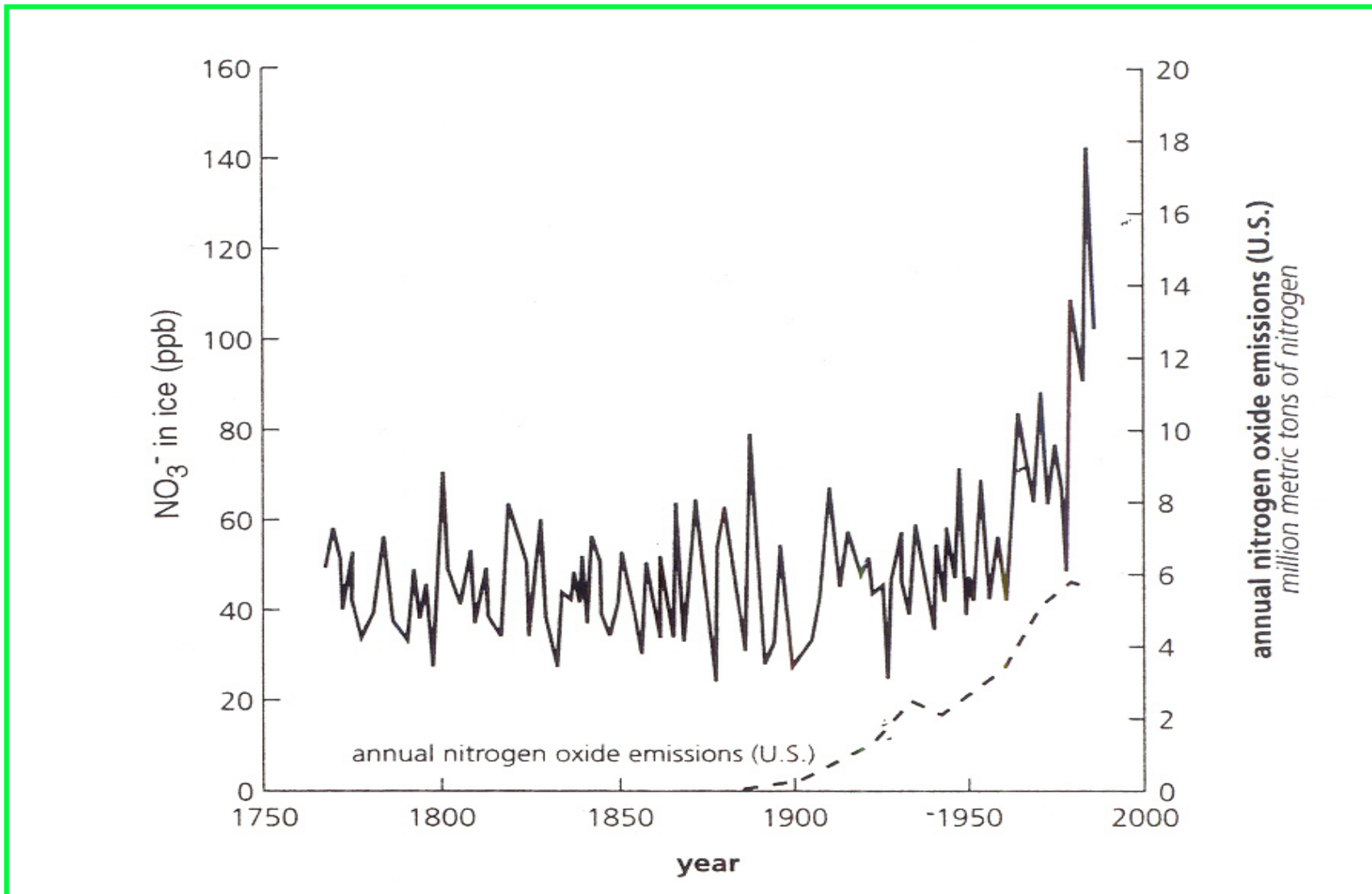
Global N cycle on the Early Earth

- Early atmosphere dominated by N_2 and CO_2

- N fixation by lightning and meteor shock waves (6 % of current rate); may have been important for origin of life

- Lack of N may have lead to early evolution of N fixers

- Denitrification important for maintaining atm N_2 level

- Unclear whether denitrification evolved before or after O_2 in atm; since denitrifiers tolerate low O_2, perhaps after

- Nitrification could only evolve after O_2 in atmosphere — the nitrification process requires O_2

- Both processes are at least 1×10^9 years old
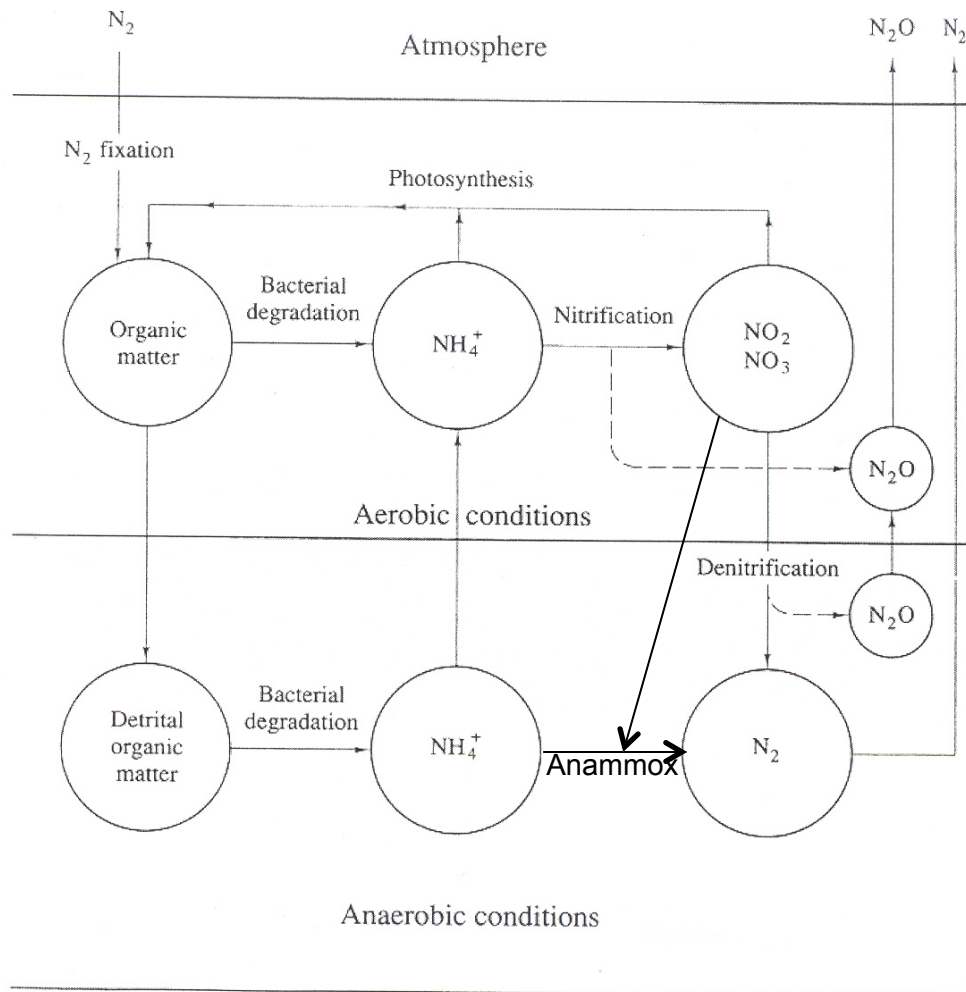
N versus P Biogeochemistry

Fig. 12.1 Schlesinger and Bernhardt 2013

- N occurs in valance states ranging from (-3) to (+5), and microbes capitalize on transformations of N from one state to another for energy

- P is almost always at a valance of (+5) as PO_4^{3-}

N versus P Biogeochemistry (cont'd.)

Reservoir	Mass N (in grams)	Mass P (in grams)
Atmosphere	3.5×10^{21}	0.00003×10^{12}
Soil Organic Matter	$95\text{-}140 \times 10^{15}$	$100\text{-}200 \times 10^{12}$
Terrestrial Biomass	3.5×10^{15}	3×10^{12}
Total oceans (NO_3^-, DIP)	570×10^{15}	93.5×10^{12}
Ocean dissolved N_2 gas	$1.1 \times 10^{19}g$	N/A
Oceanic biota	4.7×10^{14}	$0.05\text{-}0.1 \times 10^{12}$

Major Differences in Reservoirs & Fluxes:

- No gaseous forms of P, whereas $N_2(g)$ is largest N-pool

- Ultimate N Bioavailability via microbial transformations; ultimate P bioavailability via weathering

- N more enriched than P in organic matter, relative to C – C:N:P ratio in marine primary producer biomass (106:16:1)

Essential, Limiting Nutrients, N & P
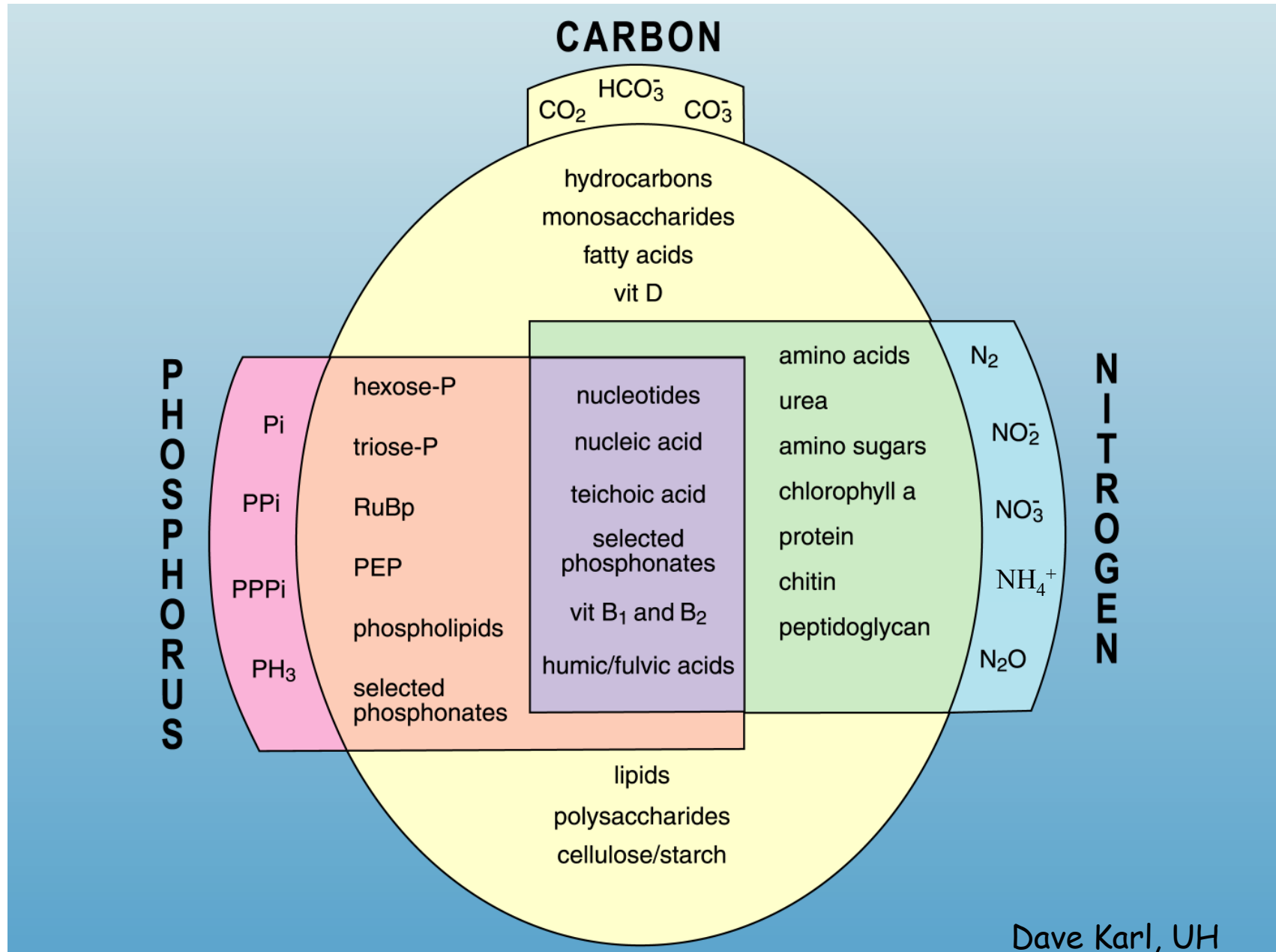
Linked N-, P-, and Carbon-Cycling

- P as ATP important in all biochemical processes, including C-fixation, protein (nitrogenous compound) production

- Primary production requires both N & P, both tend to be present at low - limiting levels

- Redfield C:N:P used to predict biomass production

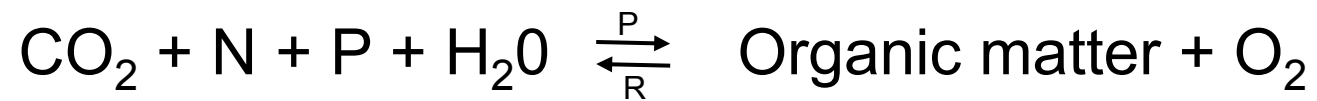- N-fixation rates inversely related to N:P in soil, lakes and the oceans
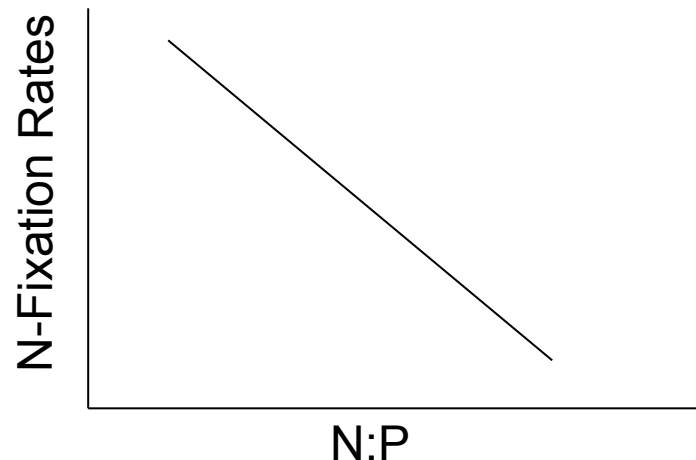
Linked N-, P-, and Carbon-Cycling
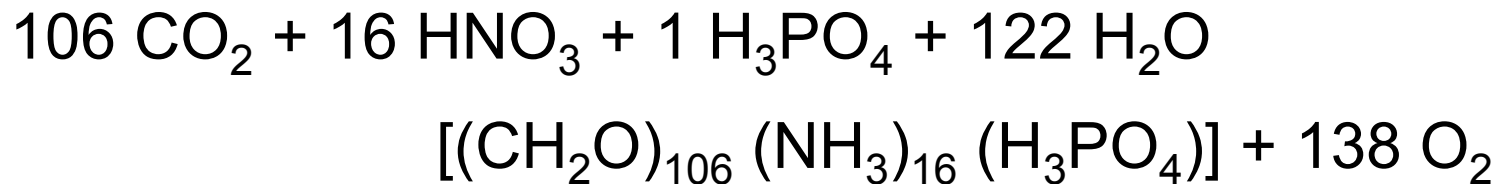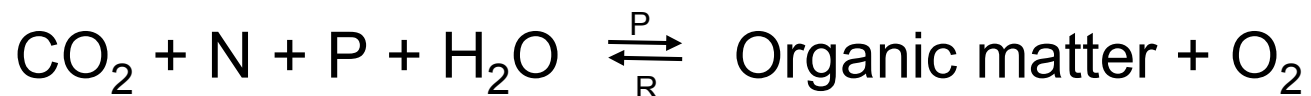
Example:

Photosynthesis and respiration

Redfield-Richards Equation:

$$CO_2 + N + P + H_2O \underset{R}{\overset{P}{\rightleftarrows}} \text{Organic matter} + O_2$$

Linked N-, P-, and Carbon-Cycling

Example:

Photosynthesis and respiration ... *Redfield-Richards Equation:*

$$CO_2 + N + P + H_2O \quad \overset{P}{\underset{R}{\rightleftharpoons}} \quad \text{Organic matter} + O_2$$

$$106\ CO_2 + 16\ HNO_3 + 1\ H_3PO_4 + 122\ H_2O$$

$$[(CH_2O)_{106}\ (NH_3)_{16}\ (H_3PO_4)] + 138\ O_2$$

Stoichiometric relationship between C, N and P via the Redfield Ratio can be used to understand linked cycles.

Linked N-, P-, and Carbon-Cycling

- High demand for P by N-fixing organisms links global C-N-P cycles: P is the ultimate limiting nutrient

- Despite this, NPP often shows an immediate response to N additions

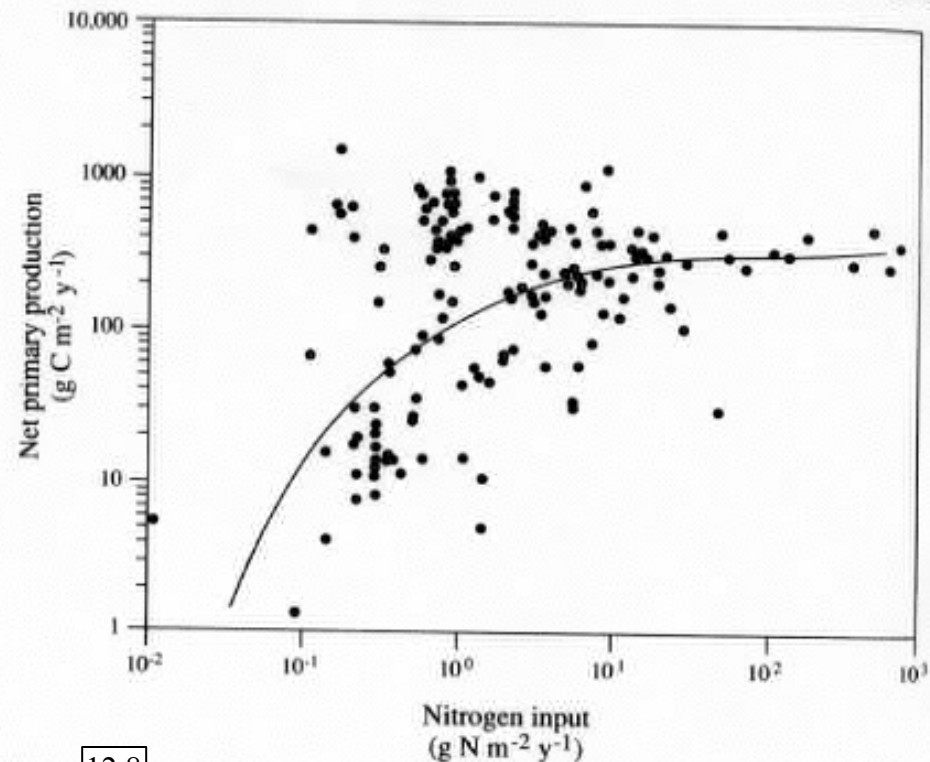- It continues to be a puzzle, and a source of debate

Figure 12.8 Net primary productivity versus nitrogen inputs to terrestrial, aquatic, and marine ecosystems. Net primary production increases in direct response to added nitrogen up to inputs of about 10 g N m^{-1} yr^{-1}. Inputs in excess of that level are rarely found in natural ecosystems, but are seen in polluted environments and agricultural soils. Modified from Levin (1989).

Summary: Nitrogen Cycle & C-N-P Linkages

- Microbial reactions drive the N cycle, taking advantage of the various valences in which N occurs in the environment

- Atmospheric N_2(gas) is the largest N-reservoir, but is inaccessible to organisms unless converted to 'fixed-N'

- Unclear whether the global N budget is balanced: Denitrification is used to balance N-fixation, but global estimates of both are not well constrained

- Anthropogenic impacts on the global N cycle have been substantial

- Nature of N & P reservoirs and processes that impact their bioavailability are fundamentally different, can be linked through stoichiometry

- Can use Redfield stoichiometry of C:N:P to predict changes in linked cycles.